Thermodynamics of Transition Metal-Rare Earth Alloys with Special Reference to Direct Alloy Production(遷移金属-希土類合金の熱力学的性質と合金直接製造法に関する研究)

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論文内容要旨

Many alloys of transition metals (TM) with rare earth metals (RE) have been found to have functional properties or be basic system of some multi−component functional materials. It is expected that such materials will play a more and more important role in the development of high technologies. On the other hand, it will be also true that the development of materials themselves requires detailed understanding of some basic properties, including the thermodynamic properties, of the TM − RE alloy systems. Efficient and economical production processes, such as reduction−diffusion(R−D) process and molten salt electrolysis with a consumptive electrode in which TM−RE mother alloy is directly produced from rare earth raw materials (oxides, chlorides, fluorides), will provide impetus to the application of the promising materials. This consideration is the starting point of the present research.

The work focuses its attention on the studies on the thermodynamic properties of TM−RE alloy systems and on the reaction mechanisms and characteristics of the reduction diffusion

(R−D) processes for producing the TM−RE alloys. The background and aim of the present study are described in Chapter 1.

Measurements of high temperature heat contents of the Cu−RE binary systems are described in Chapter 2. The heat contents of the Cu−RE (RE=Y, La, Ce, Pr, Nd) binary alloy systems were measured at temperature range of 850 to 1300 K by using a drop calorimeter. The congruent melting temperatures and heats of fusion of the intermetallic compounds (CuRE, Cu_2RE, Cu_4RE and Cu_6RE), the temperatures of other phase changes as well as the average specific heats of the liquid phases of these alloy systems were derived from the heat content data. The specific heats of the liquid phases show large, positive deviation from the Kopp−Neumann additivity−rule. The entropies of fusion of the ordered compounds were found smaller than those calculated by assuming the liquid alloys to be an ideal solution. This was considered as evidence of the existence of chemical short range order in the liquid alloys. The free energies of mixing of the liquid alloys were estimated on the basis of the experimental data and a subregular solution model.

Using the heat content and phase transformation data obtained in Chapter 2 and other thermodynamic and phase relations data reported in literatures, a thermodynamic optimization was carried out for the Cu−La and Cu−Y systems in Chapter 3. The optimization provided a set of thermodynamically consistent coefficients for each of the systems to describe the excess Gibbs free energies of the liquid solution phase as well as of the intermetallic compounds in the systems. The thermodynamic functions and the phase relations calculated for the systems using these coefficients agree well with experimental data. It is expected that the coefficients will be useful for calculating phase stability of multicomponent systems containing copper, lanthanum and yttrium, such as Cu−Sr−La−O and Cu−Y−Ba−O systems which have superconducting properties.

A phase relation and thermodynamic study of the Ni−RE binary and ternary systems are described in Chapter 4. The liquidus lines in equilibrium with the Ni_5RE compounds on the RE-rich side in the Ni−RE(RE=La, Ce, Pr, Nd) binary systems and the liquidus lines in the six ternary Ni−RE_j−RE_k (RE_j and RE_k represent any two from La, Ce, Pr and Nd) systems in equilibrium with the compounds of $Ni_5RE_{j,\theta}RE_{k,(1-\theta)}$, $0<\theta<1$, in a temperature range of 1273−1513 K were experimentally determined. The results for the Ni−Ce system agree well with the reported phase diagram. For the other three binary systems, the present results are all higher in nickel concentration when compared with the reported phase diagrams. The nickel concentrations of the liquidus lines in the Ni−La−Ce and Ni−Nd−Ce ternary systems at a

given temperature are all higher than those given by the straight lines connecting the liquidu points for the two Ni−RE binaries at the same temperature, while those for the Ni−La−Pr Ni−La−Nd and Ni−Pr−Nd systems can be well represented by such straight lines. A thermo dynamic evaluation was carried out for each of the binary and ternary systems under discus sion using the experimental data and other available thermodynamic information. A set of coef ficients to describe the excess free energy of mixing of the liquid phase and the free energy of formation of the compound phase were obtained for each system. The liquidus lines calculated for the Ni−RE binary and ternary systems using the coefficients for the respective systems agree well with the experimental data.

In Chapter 5, a study was carried out to assess the feasibility of the direct production of binary Cu−RE and Ni−RE alloys from rare earth raw materials such as oxides, chlorides and fluorides with alkali and alkaline earth metal reductants. The gas phase potentials of the reductants (Ca, Mg, Li, Na) equilibrating with the Cu−RE and Ni−RE (RE=La, Ce, Pr, Nd, Sm, Dy) alloys were calculated by using the free energies of mixing of the alloy systems obtain ed in Chapters 2 to 4. The main results obtained are summarized as follows : Due to the large negative values of free energies of mixing, the alloys may be produced with less potent reduc ing reagents than those for producing the pure rare earth metals. With Ca(1) as a reductant, all of these alloys of any composition can be produced directly from the rare earth oxide, chlo rides or fluorides. When Mg(1) is used, it is possible to produce alloys with low rare earth con centration from the raw materials. When Li(1) is used, of any composition may be obtained from the chlorides and fluorides and only the alloys with low rare earth concectration are ob tainable from the oxides. With Na alloys of any composition are obtainable from the chlorides. Alloys with moderate or low rare earth concentrations are hopeful from the fluorides and it i s impossible to make any alloy from the oxides using Na(1).

Experimental studies which were carried out on the production of Fe−RE, Co−RE (RE= Nb, Sm), Ni−La, Ni−REm (REm:misch metal) and Ni−Ti alloys with the R−D method using calcium as reductant are described in Chapter 6. The feasibility, reaction mechanism and characteristics of the R−D process were discussed on the basis of the experimental results for respective systems.

(a) the Fe−RE and Co−RE (RE=Nd, Sm) systems : In the R−D process, the alloys are formed through the diffusion of iron or cobalt into rare earths was observed. The reaction rate in the R−D process for the Fe−Nd system is independent of temperature while that for the other three systems increase with temperature. The rate determining step of the R−D process for these four systems is identified to be the diffusion of respective rare earth through the

alloy layers surrounding the pure iron or cobalt core. It was confirmed that Fe_2Nd phase does not exist in the Fe—Nd system in a temperature range of 773 to 1323 K under one atmospheric pressure.

(b) the Ni—REm systems : Calcium always exists in the products of Ni—La and Ni—REm alloys due to the fact that all of the components in these systems can form alloys with calcium. It is difficult under the experimental conditions to obtain homogeneous Ni—La(Ca) alloys due to the unavoidable existence of unreacted regions in the sample briquette, which was believed to be due to the special alloying behaviors of Ni and La with Ca. It is feasible to produce Ni—REm metal alloys containing certain amount of calcium by the R—D method.

(c) the Ni—Ti system : Ni—Ti alloys free of calcium are obtainable by the R—D method. The success is attributable to the immiscibility between titanium and calcium.

The results of these three groups of experiments show that, for a thermodynamically possible R—D process, one of the most important factors deciding the applicability of the method is the alloying behaviors of the reductant with the components of the alloy to be produced. If the reductant is undesirable as impurity in the product, then at least one of the components in the alloy system should be immiscible with the reductant.

A brief summary of the present study was given in Chapter 7, along with some consideration for further research which will be extended from the present work.

審 査 結 果 の 要 旨

遷移金属と希土類金属との合金は，磁性材料をはじめ，種々の機能材料として実用されているが，個々の合金系の性質に関する研究は未だ不十分であり，熱力学的性質についても不明確な点が多い。本論文は，CuおよびNiと各種の希土類金属との間の合金系について熱容量を直接測定し，また，相関係の解析を行うことにより，種々の熱力学パラメータを評価し，さらにこれらに基づいてCu，Niなどと希土類化合物から合金を直接製造するプロセスの可能性を理論と実験により確かめた結果をまとめたもので，全編7章よりなる。

第1章は緒論である。

第2章ではCuとY，La，Ce，Pr，Ndとの間の5種の2元合金系に対して落下型熱量計を用いて熱容量測定を行った結果について述べており，これらの合金系の比熱がKopp－Neumann則から大きく正に偏倚することを見出した。

第3章ではCu－Y，Cu－Laの2系を選び，報告されている熱力学数値や相状態図などについての情報を加えて整理し，溶融合金や金属間化合物の生成自由エネルギー値を数式としてとりまとめた。これは多元系合金に関する生成自由エネルギー値の推測の基礎として有用である。

第4章ではNiとLa，Ce，Pr，Ndとの間の4種の2元系およびこれらを組み合わせた6種の3元系合金について，金属間化合物と平衡する液相組成を種々の温度において実験的に定め，これに基づいて各合金系の混合熱，金属間化合物の生成自由エネルギー等の算出を行っている。これらの結果はNiと希土類金属との合金の高温における熱力学的性質として重要である。

第5章では酸化物，塩化物などの希土類金属原料からCa，Mg，Na等を還元剤としてCuあるいはNiとの合金を直接製造するプロセスについて，第2章，第3章および第4章で得られた熱力学パラメータを用いて可能性の検討を行った経過を述べている。その結果，Mg，Li，Naを還元剤として用いた場合には得られる合金の濃度に限界があるが，Caを用いた場合にはあらゆる濃度の希土類合金が得られることが予測された。

第6章では実用上も重要なFe－NdおよびNi－希土類系合金を直接製造法の例としてとりあげ，Caを還元剤とする還元拡散法による製造実験を行った結果について述べている。得られた合金の組織観察から均一な合金を得るためには遷移金属－希土類金属の組み合わせ，Caと合金を造るか否か，遷移金属の粒子径などの要因が重要であることを多くの例について明らかにした。これらは将来の還元拡散法の適用に肯定的な示唆を与える有用な知見である。

第7章は総括である。

以上要するに本論文は，Cu，Niなどの遷移金属と各種の希土類金属の間の数多くの合金系について熱力学的性質を明らかにするとともに，その結果に基づいてこれら合金を直接製造するプロセスについて理論的，実験的に検討し，実用への基礎を与えたもので，金属工学の発展に寄与するところが少なくない。

よって，本論文は工学博士の学位論文として合格と認める。